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The 22nd day of September 2006

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**Applicant/Proprietor:** BAYER AKTIENGESELLSCHAFT,  
51573 Leverkusen/DE

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Letang

**Process for improved preparation of graft polymers**

The present invention relates to an improved process for preparation of graft polymers of ABS type using Raman spectroscopy to detect deviations from the prescribed intended course of the reaction.

Graft polymers of ABS type are two-phase plastics composed of a thermoplastic copolymer of resin-forming monomers, e.g. styrene and acrylonitrile, and also at least one graft polymer which is obtainable via polymerization of one or more resin-forming monomers, e.g. of the abovementioned, in the presence of a rubber, e.g. butadiene homo- or copolymer, as graft base.

The expression graft polymers of ABS type also encompasses for the purposes of the present invention those constitutions in which these constituents have been replaced entirely or to some extent by analogous constituents. Examples of analogous constituents for styrene are  $\alpha$ -methylstyrene, chlorostyrene, vinyltoluene, p-methylstyrene, or tert-butylstyrene. Examples of analogous constituents for acrylonitrile are methacrylonitrile, ethacrylonitrile, methyl methacrylate, or N-phenylmaleimide. An example of an analogous constituent for butadiene is isoprene.

Graft polymers of ABS type and processes for their preparation are in principle known (see, for example, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21, VCH Weinheim, 1992). These graft polymers can, for example, be prepared via polymerization in solution or by what is known as the bulk process, or else via polymerization in the presence of water (emulsion polymerization, suspension polymerization).

In the processes known from the prior art an attempt is usually made to maximize the uniformity of the course of the reaction while keeping a maximum number of process parameters constant (e.g. temperature, monomer feed profile, pressure, etc.), and thus to obtain products whose advantageous properties have maximum reproducibility.

However, control of the process parameters does not guarantee that, on a large industrial scale, the process will be completely reproducible and that the products obtained will have prescribed properties. Many factors can affect the reaction rate profile, examples being contaminants present in the reactants, variations of stirrer speed, the nature of the surface of the reaction vessel, and variations in particle size, etc.

During graft polymerization, these causes can lead either to a decrease or to an increase in the concentration of one or more monomers in the reaction mixture.

Such a deviation of the concentration of one or more monomers from the usual concentration at a given juncture can however lead not only to product quality impairment but also to problems of reliability and safety (e.g. risk that the course of the reaction will be uncontrolled, an example being a "runaway" reaction).

The invention provides a process for improved preparation of graft polymers of ABS type by the emulsion process, by polymerizing

from 5 to 95%, preferably from 30 to 90%, by weight of a monomer mixture comprising

- A) from 50 to 99 parts by weight, preferably from 50 to 70 parts by weight, of at least one vinylaromatic
- B) from 1 to 50 parts by weight, preferably from 30 to 50 parts by weight, of at least one comonomer

in the presence of

- C) from 95 to 5% by weight, preferably from 70 to 10% by weight, of one or more graft bases with glass transition temperatures  $<10^{\circ}\text{C}$ , preferably  $<0^{\circ}\text{C}$ , particularly preferably  $<-20^{\circ}\text{C}$ ,

which comprises monitoring the course of the reaction constantly via the recording of Raman spectra of the reaction mixture and, in the event of deviations from the intended behavior, introducing corrective measures.

- 5 Corrective measures can by way of example consist in increasing or lowering the feed rate of individual monomers or of all of the monomers and/or of the initiator.

Examples of suitable vinylaromatics A) are styrene,  $\alpha$ -methylstyrene, and also ring-substituted vinylaromatics, such as p-methylstyrene and p-chlorostyrene, and also  
10 mixtures of these monomers.

Examples of suitable comonomers B) are vinyl cyanides (unsaturated nitriles), such as acrylonitrile and methacrylonitrile and/or C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylates (e.g. methyl methacrylate, n-butyl acrylate, tert-butyl acrylate), and/or derivatives (such as  
15 anhydrides and imides) of unsaturated carboxylic acids (e.g. maleic anhydride and N-phenylmaleimide).

Preferred monomers A) are those selected from at least one of the monomers styrene and  $\alpha$ -methylstyrene, and preferred monomers B) are those selected from at least one  
20 of the monomers acrylonitrile, N-phenylmaleimide, and methyl methacrylate.

Particularly preferred monomers are A) styrene and B) acrylonitrile.

Examples of suitable graft bases C) are diene rubbers, EP(D)M rubbers, i.e. those  
25 based on ethylene/propylene and, if appropriate, diene, other examples being acrylate rubbers, polyurethane rubbers, silicone rubbers, chloroprene rubbers, and ethylene-vinyl acetate rubbers, and also mixtures thereof.

Suitable acrylate rubbers of C) are preferably polymers composed of alkyl acrylates,  
30 if appropriate with up to 40% by weight, based on C) of other polymerizable, ethylenically unsaturated monomers. Among the preferred polymerizable acrylates are C<sub>1</sub>-C<sub>8</sub>-alkyl esters, such as methyl, ethyl, butyl, n-octyl, and 2-ethylhexyl esters;

haloalkyl esters, preferably halo-C<sub>1</sub>-C<sub>8</sub>-alkyl esters, such as chloroethyl acrylate, and also mixtures of these monomers.

5 Examples of preferred other polymerizable, ethylenically unsaturated monomers which can, if appropriate, be used alongside the acrylates for preparation of the graft base C) are acrylonitrile, styrene,  $\alpha$ -methylstyrene, acrylamides, vinyl C<sub>1</sub>-C<sub>6</sub>-alkyl ethers, methyl (meth)acrylate, butadiene. Rubbers preferred as graft base C are emulsion polymers whose gel content is at least 30% by weight.

10 For the preparation of acrylate rubbers, monomers having more than one polymerizable double bond can be copolymerized for crosslinking purposes. Preferred examples of crosslinking monomers are esters of unsaturated monocarboxylic acids having from 3 to 8 carbon atoms and of unsaturated monohydric alcohols having from 3 to 12 carbon atoms, or of saturated polyols  
15 having from 2 to 4 OH groups and from 2 to 20 carbon atoms, e.g. ethylene glycol dimethacrylate, allyl methacrylate; polyunsaturated heterocyclic compounds, such as trivinyl and triallyl cyanurate; polyfunctional vinyl compounds, such as di- and trivinylbenzenes; and also triallyl phosphate and diallyl phthalate.

20 Preferred crosslinking monomers are allyl methacrylate, ethylene glycol dimethacrylate, diallyl phthalate, and heterocyclic compounds which have at least three ethylenically unsaturated groups.

Particularly preferred crosslinking monomers are the cyclic monomers triallyl  
25 cyanurate, triallyl isocyanurate, triacryloylhexahydro-s-triazine, triallylbenzenes. The amount of the crosslinking monomers is preferably from 0.02 to 5% by weight, in particular from 0.05 to 2% by weight, based on the graft base C.

In the case of cyclic crosslinking monomers having at least three ethylenically  
30 unsaturated groups, it is advantageous to limit the amount to below 1% by weight of the graft base C.

Other suitable graft bases of C) are silicone rubbers having sites active for grafting purposes, as described in DE-A 37 04 657, DE-A 37 04 655, DE-A 36 31 540, and DE-A 36 31 539.

- 5 Preferred graft bases C) are diene rubbers (e.g. based on butadiene, isoprene, etc.) or are mixtures of diene rubbers, or are copolymers of diene rubbers or of their mixtures with other copolymerizable monomers (e.g. of A and B), with the proviso that the glass transition temperature of component C is below 10°C, preferably <0°C, particularly preferably <-10°C.

10

Pure polybutadiene rubber is particularly preferred as graft base C).

The gel content of the graft base C) is at least 30% by weight, preferably at least 40% by weight. The gel content of the graft base C) is determined at 25°C in toluene  
15 (M. Hoffmann, H. Krömer, R. Kuhn, Polymeranalytik I and II [Polymer Analysis I and II], Georg Thieme-Verlag, Stuttgart 1977).

The median particle size ( $d_{50}$  value) of the graft base C is generally from 0.05 to 10  $\mu\text{m}$ , preferably from 0.1 to 5  $\mu\text{m}$ , particularly preferably from 0.2 to 1  $\mu\text{m}$ .

20

The median particle size  $d_{50}$  is the diameter at which 50% by weight of the particles lie above that diameter and 50% by weight of the particles lie below. It can be determined by means of ultracentrifuge measurement (W. Scholtan, H. Lange, Kolloid, Z. and Z. Polymere 250 (1972), 782-796).

25

The graft copolymers are prepared via free-radical emulsion polymerization.

The graft polymerization can be carried out by any desired method of addition, and is preferably carried out in such a way that the monomer mixture comprising A) and B)  
30 is continuously added to the graft base C) and polymerized.

Specific monomer/rubber ratios are maintained here. The conduct of the inventive process for production of graft polymers, the monomers can be added to the rubber

latex uniformly over a defined period or using any desired metering gradients, for example in such a way that, based on the entirety of the monomers to be used during the graft polymerization, from 55 to 90% by weight, preferably from 60 to 80% by weight, and particularly preferably from 65 to 75% by weight, are fed within the first  
5 half of the total monomer feed time; the remaining proportion of monomer is fed within the second half of the total monomer feed time.

The emulsifier used can comprise conventional anionic emulsifiers, such as alkyl sulfates, alkylsulfonates, aralkylsulfonates, soaps of saturated or unsaturated fatty  
10 acids, or else of alkaline disproportionated or hydrogenated abietic or tall oil acids. It is also possible in principle to use emulsifiers having carboxyl groups (e.g. emulsifiers of DE-A 36 39 904 and DE-A 39 13 509 and disproportionated abietic acid, and salts of C<sub>10</sub>-C<sub>18</sub> fatty acids).

15 Molecular weight regulators can also be used during the graft polymerization, their amounts preferably being from 0.01 to 2% by weight, particularly preferably from 0.05 to 1% by weight (based in each case on the total amount of monomer). Examples of suitable molecular weight regulators are alkyl mercaptans, such as n-dodecyl mercaptan, tert-dodecyl mercaptan; dimeric  $\alpha$ -methylstyrene; terpinols.

20 Initiators that can be used are inorganic and organic peroxides, e.g. H<sub>2</sub>O<sub>2</sub>, di-tert-butyl peroxide, cumene hydroperoxide, dicyclohexyl percarbonate, tert-butyl hydroperoxide, p-menthane hydroperoxide, azo initiators, such as azobisisobutyronitrile, inorganic persalts, such as ammonium persulfate, sodium  
25 persulfate, or potassium persulfate, potassium perphosphate, sodium perborate, and also redox systems.

Redox systems are generally composed of an organic oxidant and of a reducing agent, and in the reaction medium there may also be heavy metal ions present here  
30 (see Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Volume 14/1, p. 263 to 297).



The polymerization temperature is generally from 25°C to 160°C, preferably from 40°C to 90°C.

5 A conventional temperature profile can be used here, e.g. an isothermal profile; however, the conduct of the graft polymerization is preferably such that the temperature difference between start and end of the reaction is at least 10°C, preferably at least 15°C, and particularly preferably at least 20°C.

10 Graft copolymers particularly preferably obtainable via the inventive process are ABS, as described by way of example in DE-A 20 35 390 (=US-A 3,644,574) or in DE-A 22 48 242 (=GB-A 1 409 275) or Ullmanns Enzyklopädie der Technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], Vol. 19 (1980), p. 280 et seq.

15 Other particularly suitable graft copolymers are ABS polymers which are prepared via persulfate initiation or via redox initiation using an initiator system composed of organic hydroperoxide and ascorbic acid as in US-A 4,937,285.

20 When graft polymers of the ABS type are prepared by the inventive process, the graft reaction is advantageously terminated when monomer conversion is from 95% to 100%.

25 In one preferred embodiment, the proportion of unpolymerized vinylaromatic component A) in the reaction mixture is less than 12% by weight at every juncture, preferably less than 10% by weight, and particularly preferably less than 9% by weight.

30 In one preferred embodiment of the invention, in order to be sure that the proportion of unpolymerized vinylaromatic component A) does not exceed the maximum values mentioned (or that the proportion of another monomer does not move outside the desired range), these monomer concentrations are monitored in-line or on-line by means of Raman spectroscopy. For the purposes of the present invention, on-line indicates a procedure in which a proportion of the reaction mixture is diverted from

the reaction vessel for example via a side loop, and is tested, and then is reintroduced into the reaction mixture. In-line means that the measurement takes place directly in the reaction vessel.

- 5 To this end, Raman spectra of the reactor contents are recorded at short intervals during the graft polymerization in the range from  $\nu_{\min} = -4000 \text{ cm}^{-1}$  (Anti-Stokes region) and  $\nu_{\max} = 4000 \text{ cm}^{-1}$  (Stokes region), preferably  $\nu_{\min} = 500 \text{ cm}^{-1}$  and  $\nu_{\max} = 2500 \text{ cm}^{-1}$ , particularly preferably  $\nu_{\min} = 750 \text{ cm}^{-1}$  and  $\nu_{\max} = 1800 \text{ cm}^{-1}$ . The frequency of the recorded measurements depends on the speed of the stream of  
10 process data. The values are usually recorded at intervals of from 1 second to 30 minutes, preferably from 10 seconds to 10 minutes.

- In principle, any of the commercially available Raman spectrometer systems are suitable for recording the spectra, preference being given to Fourier-transform and  
15 dispersive Raman spectrometers.

- In one preferred embodiment, the monomer concentrations under consideration are calculated by the weighted subtraction method as described below from the Raman spectra measured.

- 20 The factors  $f_i$  are calculated from the following Raman spectra previously measured and stored in digitalized form in an EDP unit:  $I_{PB}(\nu)$  of polybutadiene (PB),  $I_{PS}(\nu)$  of polystyrene (PS),  $I_{PAN}(\nu)$  of polyacrylonitrile (PAN),  $I_{STY}(\nu)$  of styrene (STY) and  $I_{ACN}(\nu)$  of acrylonitrile (ACN) and from the current spectrum  $I(\nu)$  of the reactor  
25 contents, using the following condition:

- $$\sum_{\nu_{\min}}^{\nu_{\max}} \{I_K(\nu) - [f_{PB} * I_{PB}(\nu) + f_{PS} * I_{PS}(\nu) + f_{PAN} * I_{PAN}(\nu) + f_{STY} * I_{STY}(\nu) + f_{ACN} * I_{ACN}(\nu) + f_K]\}^2$$
- 30  $\nu_{\min}$   
= minimum

the summation taking place across all of the data points of the spectra  $I_i(\nu)$  digitalized in identical form.

The factors  $f_i$  are used to calculate the following quotients:

5

$$Q_{PS} = f_{PS}/f_{PB}, Q_{PAN} = f_{PAN}/f_{PB}, Q_{STY} = f_{STY}/f_{PB} \text{ and } Q_{ACN} = f_{ACN}/f_{PB}$$

and the previously determined calibration factors  $K$  are used to calculate the quantitative proportions  $W$  of:

10

polystyrene with respect to polybutadiene:  $W_{PS} = K_{PS} * Q_{PS}$

polyacrylonitrile with respect to polybutadiene:  $W_{PAN} = K_{PAN} * Q_{PAN}$

styrene with respect to polybutadiene:  $W_{STY} = K_{STY} * Q_{STY}$

acrylonitrile with respect to polybutadiene:  $W_{ACN} = K_{ACN} * Q_{ACN}$

15

and the absolute amounts of polystyrene  $M_{PS}$ , polyacrylonitrile  $M_{PAN}$ , styrene  $M_{STY}$  and acrylonitrile  $M_{ACN}$  in the reactor are determined as follows:

$$M_{PS} = W_{PS} * M_{PB}, M_{PAN} = W_{PAN} * M_{PB}, M_{STY} = W_{STY} * M_{PB} \text{ and } M_{ACN} = W_{ACN} * M_{PB}.$$

20

The variable  $M_{PB}$  is constant during the reaction. The amount of polybutadiene fed into the reactor is to be detected by means of conventional quantitative measurement.

In one particularly preferred embodiment, the factors  $K_{PS}$ ,  $K_{PAN}$ ,  $K_{STY}$  and  $K_{ACN}$  are determined in an upstream calibration step by recording the Raman spectra  $I_K(\nu)$  of mixtures with known quantitative proportions. The factors  $f_i$  are calculated (weighted subtraction) by using the following condition:

$$\sum_{\nu_{\min}}^{\nu_{\max}} \{I_K(\nu) - [f_{PB} * I_{PB}(\nu) + f_{PS} * I_{PS}(\nu) + f_{PAN} * I_{PAN}(\nu) + f_{STY} * I_{STY}(\nu) + f_{ACN} * I_{ACN}(\nu) + f_k]\}^2 = \text{minimum}$$

and these are used to calculate the following quotients:

$$Q_{PS} = f_{PS}/f_{PB}, Q_{PAN} = f_{PAN}/f_{PB}, Q_{STY} = f_{STY}/f_{PB} \text{ and } Q_{ACN} = f_{PAN}/f_{PB},$$

5 and the known quantities M are used to calculate the parts by weight W

$$W_{PS} = M_{PS}/M_{PB}, W_{PAN} = M_{PAN}/M_{PB}, W_{STY} = M_{STY}/M_{PB} \text{ and } W_{ACN} = M_{ACN}/M_{PB}$$

and the calibration factors K are calculated from the following equations:

10

$$K_{PS} = W_{PS}/Q_{PS}, K_{PAN} = W_{PAN}/Q_{PAN}, K_{STY} = W_{STY}/Q_{STY} \text{ and } K_{ACN} = W_{ACN}/Q_{ACN}.$$

The inventive process features improved reliability and safety of the reaction during the entire course of the graft polymerization process.

15

The graft polymers obtainable via the inventive process feature very good mechanical properties (such as good notched impact resistances) with very high reproducibility.

20 These graft polymers are suitable, preferably after blending with at least one rubber-free resin component, for production of moldings, for example for household devices, motor vehicle components, office machines, telephones, radio casings, television casings, furniture, pipes, leisure items, or toys.

25 The rubber-free resin components used preferably comprise copolymers of styrene and of acrylonitrile in a ratio by weight of from 95:5 to 50:50, and styrene and/or acrylonitrile here can be replaced entirely or to some extent by  $\alpha$ -methylstyrene, methyl methacrylate, or N-phenylmaleimide. Particularly preferred copolymers are those whose proportions of incorporated acrylonitrile units are below 30% by weight.

30

The weight-average molecular weights  $\bar{M}_w$  of these copolymers are preferably from 20 000 to 200 000 and their intrinsic viscosities  $[\eta]$  are preferably from 20 to 110 ml/g (measured in dimethylformamide at 25°C).

Details of preparation of these copolymers are described by way of example in DE-A 24 20 358 and DE-A 27 24 360. Vinyl resins prepared via bulk or solution polymerization have proven particularly successful. The copolymers can be added alone or in any desired mixture.

5

Materials that can also be used as rubber-free resin components in the inventive molding compositions, other than thermoplastic resins composed of vinyl monomers, are polycondensates, e.g. aromatic polycarbonates, aromatic polyester carbonates, polyesters, polyamides.

10

Examples are used below to illustrate the invention, but the invention is not restricted to these examples.

**Example 1**

(Inventive, simulation of a failure of initiator feed with constant monitoring via recording of Raman spectra and corrective measures in the event of deviations from the intended behavior)

42 parts by weight of a monomer mixture composed of styrene and acrylonitrile (ratio by weight 67.5 : 32.5) and 0.15 part by weight of tert-dodecyl mercaptan are metered within a period of 6 h at 62°C into 58 parts by weight (calculated as solid) of a polybutadiene latex (solids content about 30% by weight, median particle size  $d_{50}$  about 350 nm). In parallel with this, 16.2 parts by weight of a 7.4% aqueous emulsifier solution (sodium salt of Dresinate 731<sup>®</sup> from Abieta Chemie, Gersthofen, Germany) are fed. The course of the reaction is constantly monitored via recording of Raman spectra. Once the Raman spectra have indicated a rise in the amount of monomeric styrene in the reaction mixture to above 8% by weight (based on polybutadiene), the monomer feed is stopped and 0.25 part by weight of potassium persulfate (in the form of a 2.5% strength aqueous solution) is added. Once the content of monomeric styrene in the reaction mixture has fallen below 6% by weight (based on polybutadiene), the monomer feed is continued and a 3-hour feed of 0.25 parts by weight of potassium persulfate (in the form of a 2.5% strength aqueous solution) is begun.

The total reaction time is 9 h (6 h reaction time + 3 h of continued-stirring time at 70°C), and fig. 1 shows the course of the reaction (determined by way of Raman spectroscopy).

**Example 2**

(Comparative experiment, simulation of a failure of initiator feed without constant monitoring via recording of Raman spectra and without corrective measures in the event of deviations from the intended behavior).

Experiment 1 is repeated, but the rise in the amount of monomeric styrene in the reaction mixture takes place as far as 20% by weight (based on polybutadiene) before the polymerization is initiated via addition of potassium persulfate solution. There was no alteration of the other reaction conditions. An illustration of the course of the reaction (detected by way of Raman spectroscopy) is shown in fig. 2.

### **Example 3**

(Comparative experiment, simulation of the course of a reaction without failure of initiator feed, reference experiment for desired course of reaction)

Experiment 1 is repeated, but from the start in parallel with the monomer feed a feed of potassium persulfate solution takes place. There is no alteration to the other reaction conditions.

An illustration of the course of the reaction (detected by way of Raman spectroscopy) is shown in fig. 3.

### **Investigation and testing of the products resulting from examples 1 to 3**

Latex specimens are removed for characterization by electron microscopy and are examined after osmium tetroxide contrasting. The morphologies shown in figures 4, 5 and 6 show that a morphology (fig. 4, product from example 1, uniform graft shell) corresponding to that of the reference experiment (fig. 6, product from example 3) is obtained only when the course of the reaction is monitored via Raman spectroscopy and corrective measures are carried out. If there is no monitoring, and if feed failures occur, the product produced has a non-uniform graft shell (fig. 5, product from example 2).

The graft rubber latices resulting from examples 1 to 3 were in each case precipitated with a magnesium sulfate/acetic acid mixture after addition of a phenolic antioxidant, and then the resultant graft powder was washed with water and dried at 70°C in a drying cabinet.

These graft rubber powders were used in an internal mixer to prepare the mixtures stated in table 1 and these were processed to give test specimens via injection molding.

- 5 The fine-particle graft rubber used here comprised a product with 50% by weight polybutadiene content and with an amount of 50% by weight of grafted-on styrene-acrylonitrile copolymer (styrene:acrylonitrile ratio 73:27) with median particle diameter  $d_{50}$  of about 120 nm.
- 10 The SAN resin used comprised a product whose average molecular weight  $\bar{M}_w$  was about 85 000 (styrene:acrylonitrile ratio 72:28).

All of the compounded materials comprised, as additives, 2 parts by weight of ethylenediaminebisstearoylamide and 0.15 part by weight of a silicone oil.

15

Notched impact resistance at room temperature ( $a_k^{RT}$ , unit: kJ/m<sup>2</sup>) was determined to ISO 180/1A, and thermoplastic flowability (MVI, unit: cm<sup>3</sup>/10 min) was determined to DIN 53 735 U.

- 20 The test values likewise stated in table 1 show that when the graft rubber prepared according to the invention is used the resultant product properties are very similar to those of the reference material.



**Table 1:** Constitutions and test data for the molding compositions investigated

Graft rubber from example 1 [parts by weight]	Graft rubber from example 2 [parts by weight]	Graft rubber from example 3 [parts by weight]	Fine-particle graft rubber [parts by weight]	SAN resin [parts by weight]	$a_kRT$ (kJ/m <sup>2</sup> )	MVR (cm <sup>3</sup> /10 min)
18	-	-	12	70	16.6	35.4
-	18	-	12	70	14.9	34.5
-	-	18	12	70	16.0	36.3

**What is claimed is:**

1. A process for preparation of graft polymers of ABS type by the emulsion process, by polymerizing
- 5 from 5 to 95% by weight of a monomer mixture comprising
- A) from 50 to 99 parts by weight of at least one vinylaromatic
- B) from 1 to 50 parts by weight of at least one comonomer
- 10 in the presence of
- C) from 95 to 5% by weight of one or more graft bases with glass transition temperatures  $<10^{\circ}\text{C}$ ,
- 15 which comprises monitoring the course of the reaction constantly via the recording of Raman spectra of the reaction mixture and, in the event of deviations from the intended behavior, introducing corrective measures.
- 20 2. The process as claimed in claim 1, where the monomer concentrations are determined from the Raman spectra by means of weighted subtraction.
3. The process as claimed in claim 2, where the proportion of unpolymerized vinylaromatic component A) in the reaction mixture is less than 12% by weight at every juncture.
- 25 4. The process as claimed in claim 3, where the vinylaromatic A) is styrene, the comonomer B is acrylonitrile, and the graft base C) is a polybutadiene rubber.

**Process for improved preparation of graft polymers**

**A b s t r a c t**

The present invention relates to an improved process for preparation of graft polymers of ABS type using Raman spectroscopy to detect deviations from the prescribed intended course of the reaction.

Fig. 1

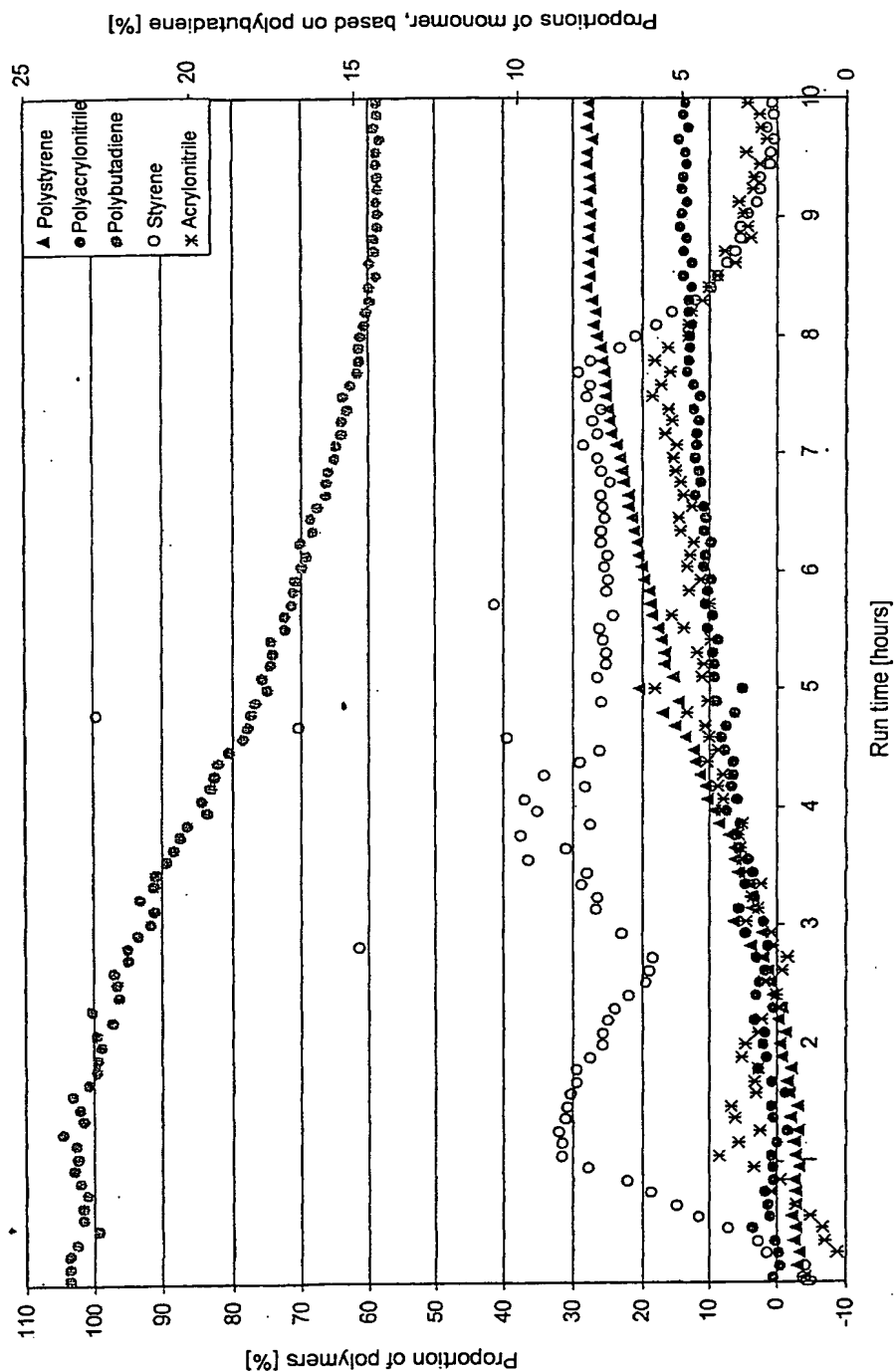


Fig. 2

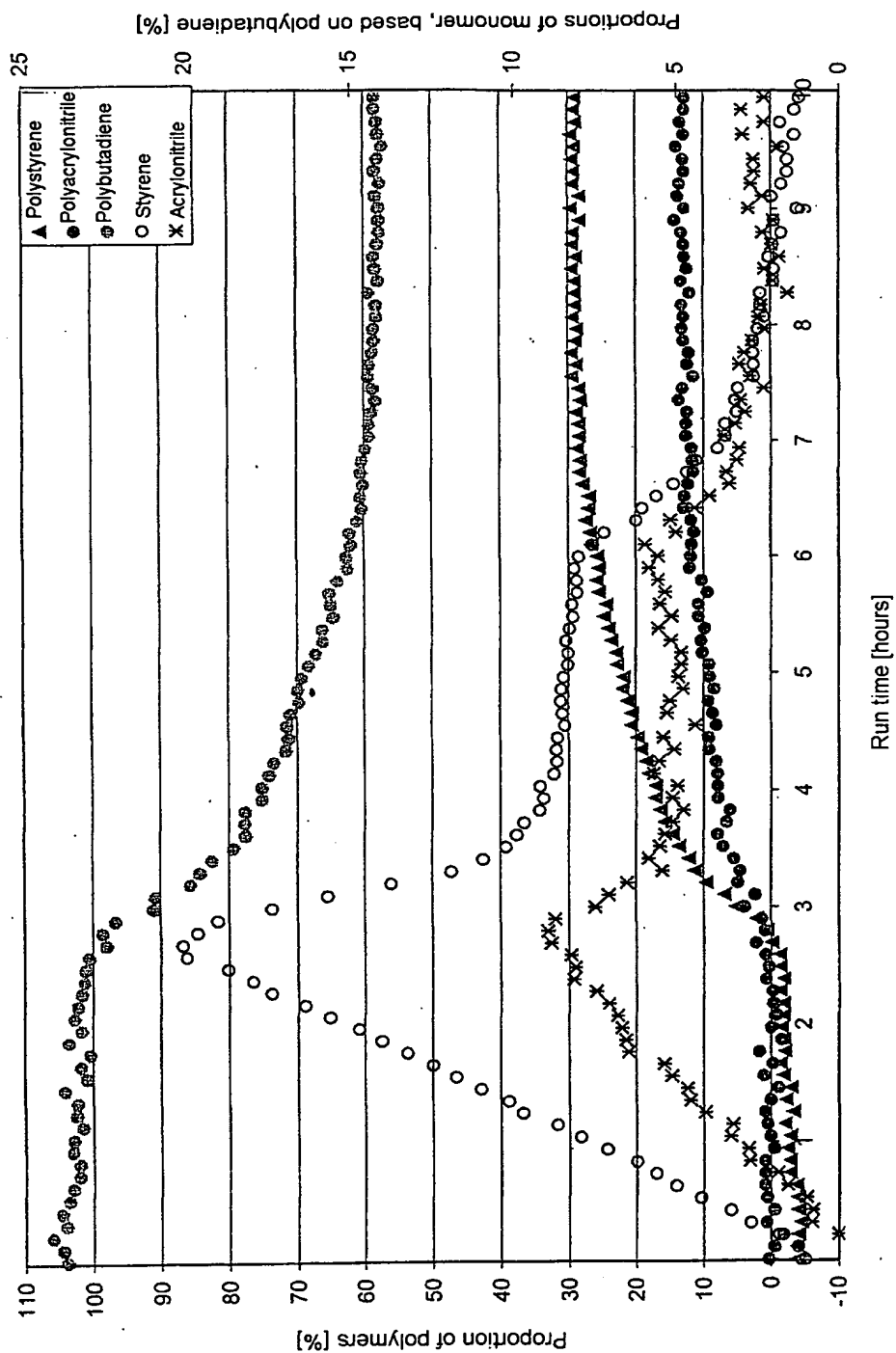


Fig. 3

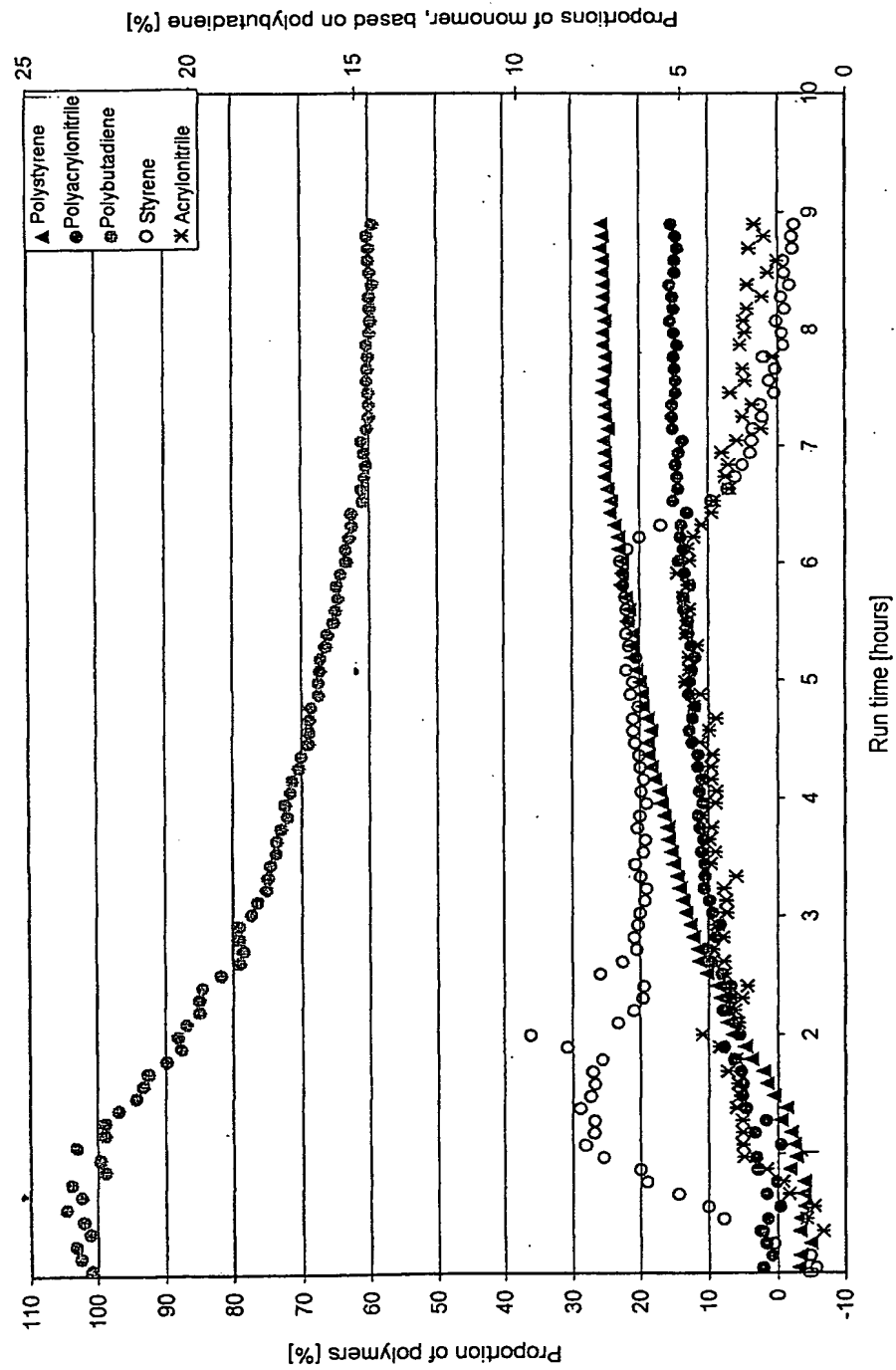


Fig. 4

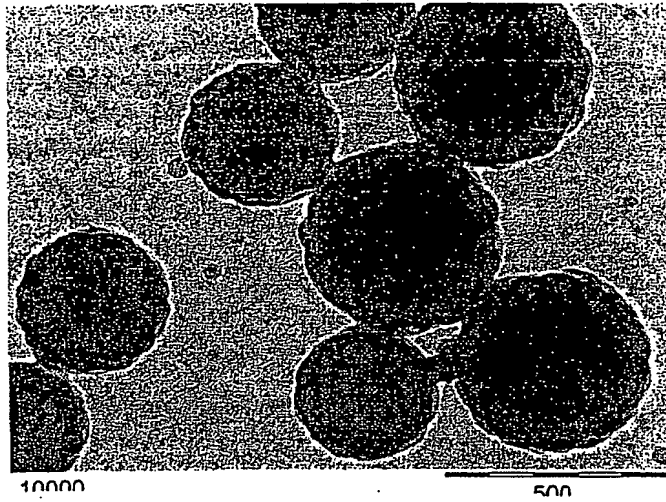


Fig. 5

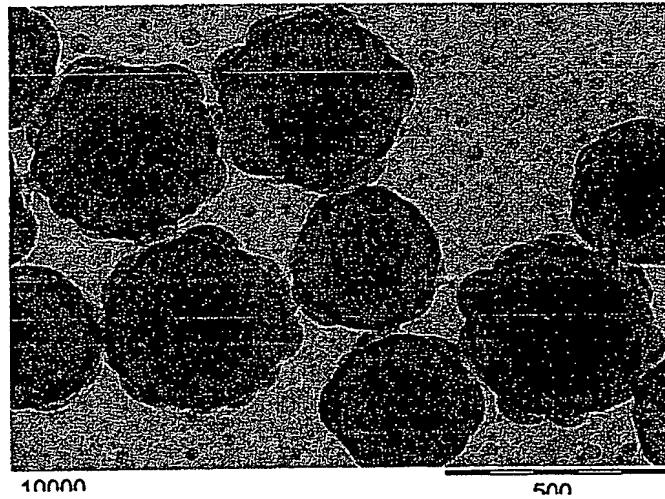


Fig. 6

